ORGANOPHOSPHORUS INSECTICIDE DECONTAMINANT

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Abstract

An organophosphorus insecticide decontaminating solution has been developed that can be used on and around aircraft and spray equipment. This solution converts the insecticides to products which can be disposed of by water washing without the extremely toxic effects to fish normally exhibited by the unaltered insecticides. The solvent component of this decontaminant is dipropylene glycol monomethyl ether (DPGME), a water-soluble, nonhazardous substance used in numerous commercial products. The active ingredient is monoethanolamine (MEA), which is also a common industrial chemical. Twenty-five percent by volume of MEA is the optimum concentration to neutralize O,O-dimethyl S-bis(carbethoxy) ethyl phosphorodithioate (malathion), while half this concentration is used to neutralize the nonsulfur-containing insecticide 1,2-dibromo-2,2-dichloroethyl dimethyl phosphate (naled), to prevent an excessive temperature increase caused by the exothermic reaction.

Introduction

The organophosphorus insecticides have rapidly gained public acceptance because of their wide spectrum of insecticidal effectiveness and the ease at which they can be degraded by environmental factors such as soil, water and vegetation. These insecticides normally do not persist in the environment more than several weeks, whereas chlorinated insecticides such as DDT persist for years, even under adverse environmental conditions.

The effective, nonpersistent nature of organophosphorus insecticides makes them ideal for both civilian and military insecticide programs; however, formulations of the highly active concentrates of these insecticides for ultra-low-volume aerial applications and other applications require special precautions during filling and handling operations. To reduce the risk of accidental exposure of workers and avoid environmental pollution, a rapid-acting, noncorrosive decontaminating solution is highly desirable when working with insecticide concentrates.

For the toxicity studies in this investigation, malathion was used as a representative for the sulfur-containing insecticides, while naled was chosen to represent the nonsulfur-containing, highly reactive insecticides. In both insecticides, the parent compounds are highly toxic to fish and related aquatic life.

Materials and Methods

Insecticides used in this study were malathion, technical (95%), American Cyanamid Co.; naled, technical (85%), Chevron Chemical Co.; dichlorvos, technical grade, Shell Chemical Co.; fenthion, technical (93%), Chemagro Corp.; and TEPP, technical (100% active ingredients), Miller Chemical and Fertilizer Corp. Chemicals used in the decontaminating solution were dipropylene glycol monomethyl ether, reagent grade, Dow Chemical Co., and purified monoethanolamine from Fisher Scientific Co. Chemicals for the extraction procedure included hexanes (Fisher Scientific Co.), certified for pesticide residue analysis, a saturated U.S.P. grade sodium chloride solution, and anhydrous sodium sulfate, certified ACS grade. Thin-layer chromatograms were developed with chloroform, N.F. grade, Fisher Scientific Co. Silica gel G for thin-layer chromatography was obtained from American Optical Co.

Decontamination Procedure

Insecticides were exposed to the decontaminating solution in a volume-to-volume ratio of 10 parts decontaminant to one part insecticide. For the decontamination of naled, solutions containing 12.5% MEA were used. Solutions formulated with 25% MEA were used to decontaminate malathion, dichlorvos, and fenthion. The reactions were allowed to proceed at room temperature for 30, 60, 120, and 240 minutes. At the end of each time period, the unaltered insecticides were extracted and assayed by gas chromatography and thin-layer chromatography. All experiments were performed in triplicate.

Extraction Procedure

The decontamination mixture was added to 50 ml distilled water in a 250-ml separatory funnel. The unaltered insecticides were

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extracted from the aqueous mixture with 30 ml hexanes which were added in 10-ml aliquots. To aid in the separation of the hexanes and aqueous layers, 15 ml of a saturated sodium chloride solution were added. The hexanes layer was placed over 10 grams anhydrous sodium sulfate. The extract was filtered and stored at 5°C if the sample could not be readily analyzed on the gas chromatograph. To test the efficiency of the extraction scheme, insecticides were exposed to dipropylene glycol monomethyl ether in the absence of MEA. This mixture was subjected to the same extraction procedure as the decontaminated mixture.

Gas Chromatography

Gas-liquid chromatography was used for the detection of unaltered insecticides. A Tracor MT-220 gas chromatograph equipped with a flame photometric detector was employed. A 6 foot by 1/4 inch glass column containing Chromosorb "W", 80/100 mesh, coated with 10% Dow 200 was conditioned for 48 hours at 200°C before use. This column was used for the analysis of malathion. The inlet temperature was held at 175°C, the column-oven temperature at 170°C, and the detector temperature at 190°C. For the analysis of naled, TEPP, dichlorvos and fenthion, a 6 foot by 1/4 inch glass column containing Chromosorb "G", 100/120 mesh, coated with 2% SF-96 was used. This column was conditioned at 225°C for 36 hours prior to use. The injector temperature was maintained at 185°C, the column-oven temperature at 175°C, and the detector temperature at 190°C. Gas flow rates for all gas chromatographic analyses were helium 65 cc/minute, hydrogen 180 cc/minute, oxygen 25 cc/minute, and air 90 cc/minute. Peaks obtained from the decontamination mixture extracts were compared with calibrated peaks obtained from a known concentration of insecticides in hexanes.

Thin-layer Chromatography

Glass 20 inch by 20 inch plates were coated with a 250 μ thick layer of silica gel G after the procedure of Stahl.(1) The plates were dried at room temperature, activated at 110°C for one hour and stored in a drying cabinet until needed. Chromatograms were developed in a closed tank to maintain a solvent-saturated atmosphere. The solvent front was allowed to run 18 cm from the bottom edge of the plate (16.5 cm from the starting line); this required approximately 45 minutes. After evaporation of the solvent, the plates were exposed to iodine vapors for five minutes, and all visible spots were marked. The plates were then sprayed with Hane's reagent,(2) heated at 110°C for five minutes, and exposed to ultraviolet light (3660 A). Phosphate derivatives gave yellow spots at low concentrations and blue spots at high concentrations; both increased in intensity over a three-day period.

Fish Toxicity Studies

Acute median tolerance limit (TLm) evaluations were performed in accordance with the Routine Bioassay Method.(3) The test species, mosquitofish (Gambusia affinis, Baird and Girard), was seined from ponds on Eglin AFB Reservation, Florida. The mosquitofish, total length 20-30 mm, were acclimatized in the laboratory in rectangular 10-gallon holding tanks for a minimum of 10 days before they were used. Water temperature in holding tanks and test containers was maintained at 22°C. Test animals were fed Longlife Pool Fish Food* daily. None were fasted prior to testing. Test containers were cylindrical 4.5-gallon laboratory glass jars, each housing 10 fish. Water temperature was maintained at 22°C and water depth at 250 mm. Between tests, containers were washed with detergent and rinsed with acetone. Test animals were observed hourly for the first eight hours, and at 24-hour intervals thereafter throughout the 96 hours of observation. TLm values were determined by the Reed-Muench Method.(4)

Corrosion Tests

Aluminum 7075 and 2024 strips measuring 1.0 inch by 6.0 inches by .070 inch were sanded with fine flint paper, washed with soap and water, and rinsed first with distilled water and then with acetone. The strips were oven dried for 15 minutes and weighed on an Ainsworth semi-micro balance. They were then placed in 40 ml of various solutions using 100-ml glass graduated cylinders for 96 hours for Aluminum 7075 and 144 hours for Aluminum 2024. After 96 and 144 hours, the malathion and naled samples were decontaminated using 25% MEA and 75% dipropylene glycol monomethyl ether. All samples were rewashed with soapy water, rinsed with distilled water and then with acetone, dried at 150°C for 15 minutes, and reweighed.

Samples of Aluminum 2024, 1 inch by 2 inches by 0.032 inch, and Aluminum 7075, 1 inch by 2 inches by 0.1 inch, were prepared according to the procedure previously described. The samples were placed in a solution containing 42% methanol, 53% water and 5% sodium hydroxide. Samples immersed in methanol and water served as controls. After 48 hours the samples were cleaned, dried, and reweighed.

*Longlife Fish Food Products, Division of Sternco Industries, Inc., Harrison, New Jersey.

Results and Discussion

Gas Chromatography

Gas chromatography data demonstrate that the decontaminating solution is effective in neutralizing the insecticides studied. Although neutralization rates differ widely, naled is destroyed completely after 30 minutes and most of the malathion in 60 minutes. Fenthion, one of the more stable organophosphorus insecticides, requires a higher concentration of MEA or a longer reaction period. After 240 minutes exposure to a 25% MEA solution, approximately 50% fenthion remains unaltered (Table 1).

Compound	0 min	30 min	60 min	120 min	240 min
Malathion:15% MEA in DPGME	100.00	35.0	16.9	1.3	0.3
Malathion:25% MEA in DPGME	100.00	19.6	2.4	<0.1	<0.1
Naled:12.5% MEA in DPGME	100.00	<0.1	<0.1	<0.1	<0.1
Dichlorvos:12.5% MEA in DPGME	100.00	5.3	-	-	-
Dichlorvos:25% MEA in DPGME	100.00	<0.1	<0.1	<0.1	<0.1
Fenthion:25% MEA in DPGME	100.00	77.8	63.3	57.1	48.9
TEPP:12.5% MEA in DPGME	100.00	0	0	0	0

TABLE 1. Percent insecticide remaining after exposure to decontaminating solutions.

Thin-layer Chromatography

The residual insecticide amounts determined by gas chromatography were substantiated by thin-layer chromatography. Based on the detection limits determined with standards of known concentrations, a sufficient volume of each hexane extract was applied to a single spot to allow the detection of insecticide concentrations with a lower limit of 80 ppm, corresponding to the destruction of up to 99.8% of the original amount of insecticide.

Insecticide	Detection Limit (µg)		R_F
	Iodine Vapor	Hane's reagent	
Fenthion	1.0	0.5 (blue)	85.0
Malathion	2.0	2.0 (blue)	42.5
Naled	30	3.0 (yellow) 30 (blue)	32.0
Dichlorvos	30	3.0 (yellow) 10 (blue)	24.0

TABLE 2. Thin-layer chromatography data on selected insecticides.

The qualitative and quantitative determination of insecticide in each spot was made by comparison of the R_F-value and the area of the spot with those of simultaneously developed references of known concentrations. Lowest detection limits and R_F-values for the insecticides investigated are given in Table 2. In the case of malathion, the gradual time dependent disappearance of the spot was accompanied by a corresponding appearance of others, belonging to impurities in the original malathion sample and to unidentified reaction products. These spots were visualized by iodine vapors as well as Hane's reagent and had R_F-values of 64, 56, 51.5, 22.5, 16.5, 12 (streaking), and 0.

For the reaction of dichlorvos and the 25% MEA solution, the spot corresponding to dichlorvos disappeared, while another spot with an R_F-value of 16.5 became visible after a reaction time of 30 minutes.

Fish Studies

Data obtained from fish studies indicate that the MEA decontaminating solution is highly effective in neutralizing the toxic effects of naled and malathion when 10 parts of the decontaminating solution are allowed to react with one part of the insecticide for approximately one hour. The data shown in Table 3 suggest that the mixture containing both insecticides and decontaminating solutions is less toxic to fish than the decontaminating solution alone, which already is relatively nontoxic.

Corrosion Data

Studies conducted with aircraft type Aluminum 7075 and 2024 indicate the MEA decontaminating formulations are noncorrosive to these metals relative to a dilute sodium

Compound	24 hr	48 hr	72 hr	96 hr
Malathion	4.75	4.55	4.40	3.57
Naled	1.364	1.364	1.313	1.182
25% MEA in DPGME	1840	1800	1791	1718
10:1 25% MEA in DPGME:95% malathion	2282	2182	2150	2073
10:1 12.5% MEA in DPGME:85% naled	2308	2109	2009	1945
MEA	375.00	365.90	345.31	329.16
DPGME	>8000	>8000	>8000	>8000

TABLE 3. TL_m values in ppm for mosquitofish (Gambusia affinis).

hydroxide solution, which is also capable of neutralizing organophosphorus insecticides. Samples of Aluminum 2024 and 7075 exposed to a sodium hydroxide solution had an average weight loss of 0.91725 g and 1.5453 g, respectively. The only other aluminum samples showing significant weight changes from corrosion were the ones exposed to technical grade naled (Tables 4, 5 and 6).

Kinetics of Malathion Neutralization

The decontamination of malathion appears to follow the kinetics of a second order reaction. The order of a reaction may generally be determined by substituting the observed reactant concentrations at various time intervals into a theoretical rate equation of an assumed order. If the rate constant k is found to be independent of reaction times and initial concentrations, it can be concluded that the reaction is of the same order as the one assumed. Thus, with a second order rate equation for the decontamination of malathion,

Solution	Initial Weight of Metal (g)	Final Weight of Metal (g)	Weight Difference
Malathion	24.67000	24.66867	-.00133
Malathion	24.48288	24.47959	-.00329
25% MEA in DPGME	23.71367	23.71300	-.00067
25% MEA in DPGME	24.12204	24.12133	-.00071
15% MEA in DPGME	24.74874	24.74800	-.00074
15% MEA in DPGME	24.91125	24.91051	-.00079
Malathion:25% MEA in DPGME	24.30125	24.30061	-.00064
Malathion:25% MEA in DPGME	25.26655	25.26570	-.00085
Malathion:15% MEA in DPGME	23.50300	23.50235	-.00065
Malathion:15% MEA in DPGME	24.43257	24.43194	-.00063
Naled	25.11040	25.13540	+.02500
Naled	24.78122	24.79827	+.01705
Naled:15% MEA in DPGME	25.58035	25.57984	-.00051

TABLE 4. Half immersion of Aluminum 2024 strips for 144 hours.

Solution	Initial Weight of Metal (g)	Final Weight of Metal (g)	Weight Difference
Malathion	18.82421	18.82200	-.00221
Malathion	18.75295	18.75078	-.00217
25% MEA in DPGME	18.84717	18.84593	-.00124
25% MEA in DPGME	18.81636	18.81526	-.00110
15% MEA in DPGME	18.83721	18.83665	-.00056
15% MEA in DPGME	18.76669	18.76623	-.00046
Malathion:25% MEA in DPGME	18.80413	18.80296	-.00117
Malathion:25% MEA in DPGME	18.76313	18.76282	-.00031
Malathion:15% MEA in DPGME	18.75822	18.75749	-.00073
Malathion:15% MEA in DPGME	18.62396	18.62314	-.00082
Naled	18.61326	18.62196	+.00870
Naled	18.79009	18.79500	+.00491
Naled:15% MEA in DPGME	18.74045	18.74006	-.00039
Naled:15% MEA in DPGME	18.68931	18.68947	+.00016

TABLE 5. Half immersion of Aluminum 7075 strips for 96 hours.

	Initial Weight (g)	Final Weight (g)	Weight Change
Four samples Aluminum 7075 in 42% methanol, 53% water, 5% NaOH	9.1187	7.6468	-1.4719
	9.2435	7.6700	-1.5735
	9.2331	7.7580	-1.5711
	9.3228	9.0433	-1.5648
Four samples Aluminum 2024 in 42% methanol, 53% water, 5% NaOH	2.9009	1.9304	0.9705
	2.8900	1.9273	0.9627
	2.9049	1.9426	0.9623
	2.9125	2.1390	0.7735

TABLE 6. Complete immersion of Aluminum 7075 and 2024 strips for 48 hours.

$$r = \frac{dc_{malathion}}{dt} = - k c_{malathion}\, c_{MEA} \qquad (1)$$

the corresponding integrated rate equation is

$$kt = \frac{1}{c_{o_{MEA}} - c_{o_{malathion}}} \ln \frac{(c_{o_{MEA}} - c_{o_{malathion}} + c_{malathion})\, c_{o_{malathion}}}{c_{o_{MEA}}\, c_{malathion}} \qquad (2)$$

where $c_{o_{malathion}}$ is the initial concentration of malathion (t = 0)
$c_{o_{MEA}}$ is the initial concentration of MEA
$c_{malathion}$ is the concentration of malathion at time t
c_{MEA} is the concentration of MEA at time t

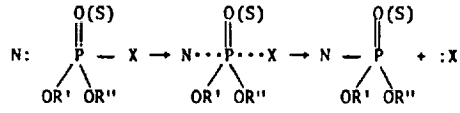
Upon substituting the observed malathion concentrations, the corresponding reaction times and the initial concentrations of MEA and malathion into equation (2), k is found to be constant within the limits of experimental error (Table 7). The neutralization of malathion is a second order reaction, with a rate constant, k, of 0.0160 l mol-1 min-1.

Having determined the appropriate rate equation and the value of the rate constant, the results of the kinetic study can be extended to other than the actual test conditions. In Figure 1, a series of curves derived from equation (2) have been plotted to predict the time required for the neutralization of 99% of a given quantity of technical grade (95%) malathion ($t_{0.99}$) as a function of the concentration of MEA in the decontaminant and the ratio of decontaminant solution to malathion. As can be seen from Figure 1, the decrease in $t_{0.99}$ becomes continuously smaller as the concentration of MEA is increased. Also, as the ratio of decontaminant to malathion goes beyond 10.1, the decrease of $t_{0.99}$ becomes negligible.

Theoretical Mechanisms

With the large variety of organophosphorus insecticides available today and more likely to be developed in the future, this study was restricted by necessity to a small number which may be considered characteristic examples of the entire class. It would be of interest if the results could be generalized to all organophosphorus insecticides, both to predict decontamination rates and to determine the toxicity of breakdown products. For this purpose, the reaction mechanism must be considered in more detail.

Most organophosphorus insecticides are esters or anhydrides of phosphoric, phosphorothioic, or phosphorodithioic acids. In these compounds, the higher electronegativity of oxygen (3.5) and sulfur (2.5) in comparison to that of phosphorus (2.1) places a positive charge on the phosphorus atom, making it the electrophilic center of the molecule. As a consequence, organophosphorus insecticides can react with nucleophilic agents by direct displacement at the phosphorus atom.



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Kinetic analysis of a large number of solvolyses of organophosphorus insecticides and their reactions with various nucleophiles has led to the conclusion that they proceed by a one-step mechanism similar to the S_N2 reaction at saturated carbon. In this type of reaction, the new bond is formed simultaneously with the breaking or, in some instances, shortly after the weakening ("S_N1" character) of the old bond. However, for the sake of clarity, the designations "S_N1" and "S_N2" should be used only for displacement reactions at saturated carbon.

MEA can be considered to be a typical nucleophile which will react with organophosphorus insecticides by the mechanism above. This has been found to be the case in the reaction of MEA and several phosphorus compounds analogous to organophosphorus insecticides.[5] It was found at the same time that for the two

t (min)	$c_{o_{MEA}}$ (mol l^{-1})	$c_{o_{malathion}}$ (mol l^{-1})	$c_{malathion}$ (mol l^{-1})	k ($l\ mol^{-1}\ min^{-1}$)
30.0	3.73	0.320	0.0628	0.0152
60.0	3.73	0.320	0.0078	0.0178
30.0	2.24	0.320	0.112	0.0164
60.0	2.24	0.320	0.0540	0.0144

TABLE 7. Calculated values for reaction constant k in decontamination of malathion.

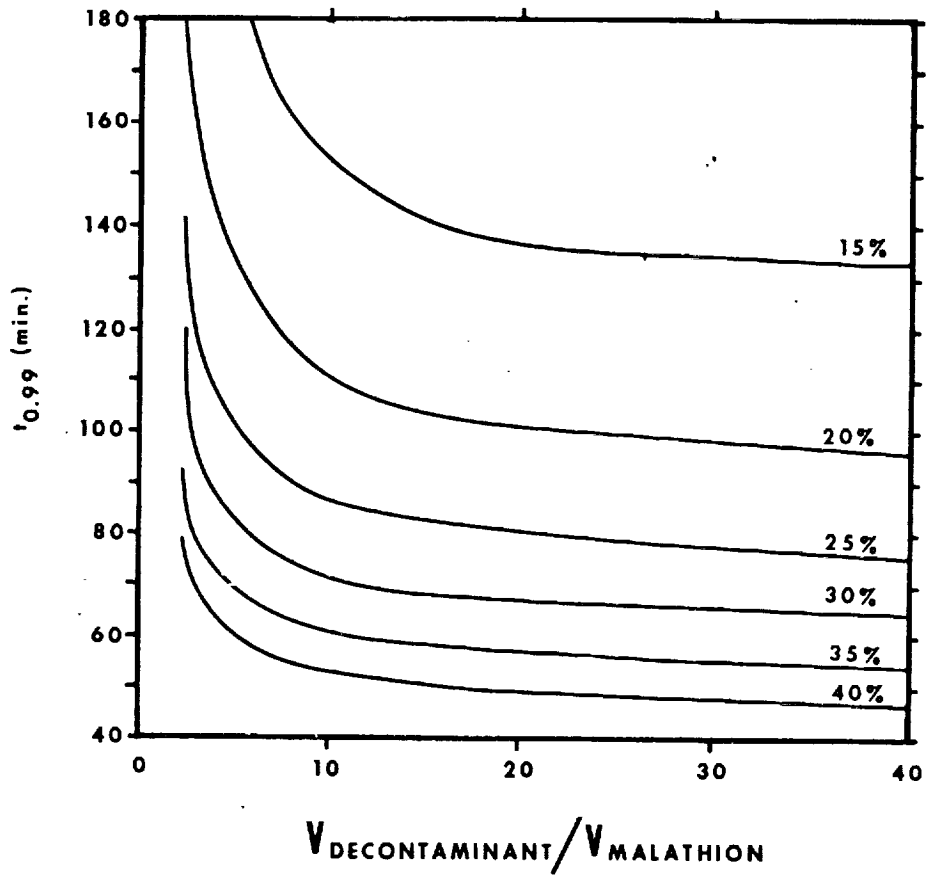

FIGURE 1. Time required to decontaminate 99% of a malathion sample as a function of ratio of decontaminant to malathion and concentration of monoethanolamine.

nucleophilic functions of MEA, the hydroxyl and the amino group, the reaction of the amino group predominates.

As to the factors which determine the reaction rate, the most important ones are steric effects and the influence of the substituents on the magnitude of the positive charge on phosphorus.[6,7] Increasing size of the substituents on the phosphorus atom will cause increasing steric hindrance in the transition state and, therefore, reduce the reaction rate. The reaction rate will also be reduced by substituents with a decreased electron-withdrawing effect. This would reduce the positive charge on phosphorus, rendering it less susceptible to nucleophilic attack. Thus, because of the difference in electronegativity between oxygen and sulfur, the reaction rate of a phosphate ester will be slower than that of the corresponding phosphorodithioate ester. The same factors appear to control the hydrolysis rates of organophosphorus insecticides, and it would therefore be expected that the relative rates of decontamination with MEA would be similar to those observed during hydrolysis.[8] However, it should be kept in mind that although the relative hydrolysis rates may be similar, the rates of neutralization with MEA are much faster than the corresponding hydrolysis rates in river or lake water. Thus, for the hydrolysis of malathion, a typical half-life (pH 6) is 26 days,[9] while for neutralization with a tenfold volume of 25% MEA, the half-life is only 12 minutes.

The major alternative to a displacement reaction at phosphorus is a chemical reaction on the substituent X which, for organophosphorus insecticides, usually is a reactive carbon-containing compound. Although oxidation reactions are unlikely

under the conditions of the decontamination, chemical reactions involving nucleophilic substitution reactions at saturated and unsaturated carbons and elimination reactions are possible. The nature and extent of the reactions depend strongly on the chemical structure of the substituent X. Since X is different for almost every organophosphorus insecticide, these reactions must be investigated in each particular case and cannot be discussed in general. Thus, for organophosphorus insecticides with substituents particularly sensitive to interactions with amino and hydroxyl functions, the decontamination rates may not correspond to predicted values.

In summary, MEA solutions can react with organophosphorus insecticides by a nucleophilic displacement reaction at phosphorus. The relative decontamination rates will be similar to the known relative hydrolysis rates. Depending on the nature of the substituent, certain exceptions may be found which will not be decontaminated by the theoretical mechanism.

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